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Title of Invention: Metal catalyst support and a method of manufacturing it

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Inventor: Hisao Matsumoto
Matsumoto Tekkan Co., Ltd.
1-3-20 Higashi Tsukaguchi-cho, Amigasaki-shi, Hyogo Pref.

Applicant: Matsumoto Tekkan Co., Ltd.
1-3-20 Higashi Tsukaguchi-cho, Amigasaki-shi, Hyogo Pref.

Agent: Hiroshi Ozeki, Patent Attorney

Specifications

1. Title of Invention:

   Metal catalyst support and a method of manufacturing it

2. Claims:

   (1) A metal catalyst support, characterized in that a metal oxide ceramic layer is formed on a heat-resistant stainless steel surface, a needle-shaped ceramic layer is deposited on and bonded with this layer, and a combustion catalyst is supported on this layer.

   (2) A metal catalyst support in accordance with Claim (1), in which, in a catalytic converter for automobile exhaust gas, the substrate described in Claim (1) is used as its monolith-type honeycomb metal support, and the combustion catalyst is supported on it.

   (3) A method of manufacturing metal catalyst supports with a needle-shaped ceramic densely formed on and compounded with its surface, characterized in that a suspension of a fine ceramic powder is applied to, or impregnated into, a heat-resistant stainless steel plate with a metal oxide ceramic layer formed on its surface; next, the plate is fired at a temperature of 1000°C or higher to form a needle-shaped ceramic; and, if necessary, the glass which forms together with this ceramic is removed.

3. Detailed Explanation of Invention:

Industrial Field of Application

This invention concerns a metal catalyst support which is used to support combustion catalysts; more specifically, it concerns a metal catalyst support which imparts the properties of a catalyst support to a heat-resistant stainless steel surface. Its purpose is to develop a catalyst support consisting of a stainless steel plate, on the surface of which needle-shaped ceramic crystals (whiskers) are densely formed, easily and with good efficiency, and a catalyst support layer with excellent resistance to separation is formed.

Prior Art

In order to reduce the CO, HC, and NOx in the exhaust gas, as a way of reducing automobile pollution, three-dimensional catalytic converters have been put into exhaust pipes. Monolith-type metal supports are one kind of support used in such catalytic converters; these supports are made by performing a lengthy, high-temperature heat treatment on heat-resistant 20Cr-5Al stainless steel, forming a dense layer of alumina whiskers on its surface. More specifically, the supports on which the alumina whiskers are formed are ordinarily pieces of foil of this stainless steel 0.05 mm thick; the alumina whiskers are precipitated on their surfaces by continuing a long heating process at 950°C for 16 hours to create the surface

condition necessary for them to function as catalyst supports. Since stainless steels with high aluminum contents in their original conditions have oxidation resistances which are too good, a very long time is required for heating them at a high temperature in order to cause the necessary quantity of alumina whiskers to be formed densely. Thus, this invention has a great drawback, for industrial purposes, in that the heat treatment expense is very great.

Problem That the Invention Is to Solve

The problem that this invention is to solve is the aforementioned drawback in conventional metal catalyst supports using this kind of heat-resistant stainless steel.

Means of Solving the Problems

This problem is solved by first forming a ceramic layer on the surface of the aforementioned stainless steel plate with a very short heat treatment, after which needle-shaped ceramic crystals (whiskers) are precipitated on this ceramic layer.

Operation and Make-up of Invention

The essential nature of this invention is that (a) a metal oxide ceramic layer is first formed on a heat-resistant stainless steel surface; (b) needle-shaped ceramic crystals (whiskers) are formed densely on this metal oxide layer (mullite whiskers are especially desirable); and (c) the material obtained by the aforementioned treatments (a) and (b) is used as a metal catalyst support, especially

for metal catalysts of the monolith type in automobile three-dimensional catalytic converters.

The processes (a) and (b) in this invention will be explained below.

Process (a)

The heat-resistant stainless steels used in this invention are ones which are widely used and are already known to be stainless steels with excellent heat resistance. Typical examples of these steels are ones containing chromium, aluminum, etc.; especially desirable ones are 20Cr-5Al, as well as 6Cr-5Al, 12Cr-1.5Si-0.5Ti, and 25Cr-20Ni stainless steels.

Many kinds of ceramics can be used as the metal oxide ceramic layer formed on this steel plate. Especially desirable ones are ceramic layers which have either chromium or alumina, or both, as their principal ingredients. When this ceramic layer is formed, the stainless steel is heated at a temperature of 850°C or higher, preferably 870°C or higher, for 4 hours or less, preferably 1-2 hours, in air; the ceramic layer is formed by oxidizing the surface. For example, when the stainless steel is 20Cr-5Al stainless steel, it is treated as is by the method described above. That is, the aluminum contained in the stainless steel is moved to the surface by this heat treatment, and it is oxidized over time, so that alumina is formed and grows on the surface; the ceramic layer is formed from this alumina.

The thickness of this ceramic layer is ordinarily 40 μm or less, preferably about 10-20 μm.

Process (b)

In this process, ceramic crystals in a whisker form are further formed on the aforementioned ceramic layer. The kind of ceramic crystal whiskers formed is not particularly limited, but silica or alumina ones, or ones having one of these as their principal ingredient, are preferable, and mullite whiskers are especially preferable. In producing these ceramic crystal whiskers, the ceramic raw material powdered needed for producing the desired ceramic crystal whiskers is selected and it is suspended or dispersed in a suitable ordinary kind of solvent water; the aforementioned products of process (a) are then impregnated with this solution, or it is applied to them. The ceramic powders used may be various materials which contain silica and/or alumina. Typical examples of them are diatomaceous earth, kaolin, various kinds of glass, various kinds of diatomaceous silicates, etc. After the application or impregnation has been performed, firing is performed at a temperature of 1000°C or higher for about 1-2 hours, and needle-shaped ceramic crystal whiskers are formed on the aforementioned ceramic layer of process (a). Since glass is sometimes produced at this time along with the whiskers, the glass may be removed by treating the product of this process with hydrogen fluoride, for example. The ceramic

needle-shaped whiskers formed by this treatment are formed incompletely on the surface of the aforementioned ceramic layer of process (a); as their growth is continued, they bond with the ceramic layer of process (a) or become integrated with it, so that the surface is covered with densely-packed needle-shaped ceramic crystal whiskers. Since the material obtained by processes (a) and (b) in this way has a ceramic layer and needle-shaped ceramic crystal whiskers formed on a heat-resistant stainless steel surface, it has an excellent resistance to separation, and this surface forms a porous texture which is the most suitable for the adhesion of the catalyst. It can fully resist repeated rapid temperature changes between high and low temperatures and has a strong resistance to mechanical vibrations; it can be used in a wide range of temperature conditions. Furthermore, it does not rust when condensation forms when the automobile engine stops and it comes into contact with water, so that it is an extremely stable and long-lasting material. Therefore, it has excellent properties as an automobile catalyst support.

Working Examples

This invention will be explained in more detail below by giving working examples.

The first working example, shown in Fig. 1, is its use as a metal catalyst support of the monolith type (1) in an automobile catalyst converter. In this case, a metal

substrate with a honeycomb structure (2), composed of a ferrite 20Cr-5Al stainless steel, resistant to high-temperature oxidation and having a small thermal expansion, is used; its thickness is 0.05 mm. Furthermore, as shown in Fig. 2, it is composed of flat plates (3) and corrugated plates (4) alternating with each other, rolled into a catalyst support substrate (5) with a tubular form, as shown in Fig. 3.

This support substrate (5) may be fixed, if desired, by spot welding, etc. This fixing is desirable, so that the support can withstand the changes caused by the subsequent heat treatments and its actual use. Means of fixing which can be used are soldering, welding, brazing, etc.

Next, the surface of this catalyst support substrate (5) is oxidized in air for 1 hour at 870°C or higher. At this time, the Al which was added at 5% to the ferrite high-temperature-oxidation-resistant stainless steel moves to the surface, under the high temperature, and concentrates there; over time, it oxidizes and crystals of alumina are produced and grow on the surface.

In the prior art, this process was continued for 16 hours, producing these alumina crystals in a sufficient quantity to serve as the catalyst support, i.e., they were produced densely. In this invention, however, the heating is stopped in a short time of 1 hour or less and the substrate is cooled. After this, if desired, it may be washed with an

acid or alkali, or the surface may be activated. This substrate (5) is then immersed in an aqueous suspension of a ceramic powder consisting of the fine powder which was made in a separate process, after which the substrate is fired for 1 hour at 1000-1350°C, producing needle-shaped mullite, which is a compound of silica and alumina, in the glass layer on the surface of the substrate (5). Next, the glass layer is removed with hydrogen fluoride, and the needle-shaped mullite only remains, as shown in Fig. 4. The needle-shaped mullite (6) produced is formed incompletely on the surface of the support substrate (5); as it continues to grow, it bonds with the alumina whiskers or becomes entwined with them, and is thus strongly integrated with them. As a result, a metal support covered with densely formed needle-shaped mullite (6) is produced.

As explained above, since heat-resistant stainless steel is used as the substrate in this invention, and a layer of needle-shaped mullite is formed integrally with it surface, it becomes a catalyst support which is extremely stable and durable, and is suitable for use in automobiles.

Furthermore, in this invention, the ceramic suspension which gets into the gaps (7) between the flat plates (3) and corrugated plates (4) forms needle-shaped mullite in such a way as to fill these gaps. Therefore, the parts of the catalyst surface in the prior art which were unused, due to the fact that it was hard for the gas being treated by the

catalyst to flow through these gaps (7), and which were thought to amount to 2-5% of the surface area, are eliminated, and by filling these gaps the whole catalyst surface is made to work effectively. Thus, the quantity of the catalyst which is needed is reduced, and the effect of substantially reducing the size of the catalytic converter is achieved. Furthermore, the tops of the aforementioned corrugated plates are firmly bonded, as though with an adhesive, to the flat plates by the needle-shaped mullite, forming a strong, heat-resistant structure.

As an example of the stainless steel used in this invention, 20Cr-5Al stainless steel with alumina (Al_2O_3) as the principal component was used above, but the kinds of stainless steel which can be used are not limited to this kind. In addition, of course, the forms of the ceramic produced can range from needle-shaped to granular, etc.

Furthermore, the ceramic needle-shaped crystals formed are not limited to mullite, a compound of silica and alumina; other compounds and compositions can also produce ceramic whiskers at low temperatures. Also, the method of removing the glass layer produced which was described above was elution with an aqueous solution of hydrogen fluoride, but one can also use other acid and alkali treatments.

Other oxidized impurities which are liberated from the ceramic formed on the stainless steel plate can also be removed at the same time as the elution treatment of the

glass layer.

If the surface area is increased in this manner, the quantity of needle-shaped mullite accumulated on the surface and the heat treatment expense are reduced, and a lower-cost metal support can be provided.

The following technical means are also included in this invention. That is, as a second working example, we will describe a cross-honeycomb metal catalyst support made of corrugated plates (30) and corrugated plates (31) which are placed on each other at an angle, as shown in Fig. 5, and rolled up.

In this structure, one or both plates are placed so that they form a specific angle with the axial direction; the plates are bonded with each other at the tips of the corrugations of the corrugated plates.

Therefore, some of the flat plates which were needed in the prior art need not be used, but, as shown in Fig. 6, one may also used flat plates (32) if desired. Fig. 7 shows the support of Fig. 6 rolled into a tubular form.

By using this form of the invention, the points of contact between the corrugated plates (30) and the corrugated plates (31) can be bonded by a means such as solder, brazing, or welding. The cost of the metal catalyst of this invention can be markedly reduced by bonding these contact points with the needle-shaped mullite produced on the surface of the metal catalyst support, or, to some

extent, by a glass layer.

The honeycomb metal catalyst support in tubular form of the prior art was formed from a large number of cells, extremely finely divided, about 1-2 mm^2 in cross sectional surface area, and the gas being treated proceeds straight through these cells, being catalytically treated by the three-dimensional catalyst supported on the cell walls. Therefore, in order to treat the gas more completely, its contact with the catalyst must be increased, so that the cells must be more finely divided or [the number of] cells must be increased, but this causes the drawbacks that the resistance during the time the gas is passing through the converter is increased, or the converter becomes larger. In addition, because of the structure, the flow of the exhaust gas and the heat of its treatment are concentrated in the central part of the tubular metal support, which is connected to the inlet of the converter.

Therefore, the load of the exhaust gas treatment is concentrated in the central part of the catalyst support and the temperature around this part becomes much higher. This not only leads to the risk of causing damage to the metal support, but there is also the drawback that the catalytic performance deteriorates.

Furthermore, because of the extremely fine division [of the cells,] it is extremely difficult for the gas passing through the catalyst to contact the parts of the catalyst in

the long joints between the flat and corrugated plates and the narrow crevices near them. That is, as much as 5-15% of the total area of the metal support holds parts of the expensive catalyst which do not function as a catalyst.

This embodiment [of this invention,] however, causes the flow of the gas, as well as it heat, to disperse, and lengthens the lifetimes of the support and the catalyst.

Since the peaks of the corrugated plates which intersect each other at an angle are the points where the plates are joined, the catalyst on the metal surface outside these junction points can make contact with the exhaust gas, and the efficiency of the catalyst is raised by 10-30% by the increase in the surface area of the metal, i.e., the surface area of the catalyst; the catalyst can also be made smaller.

The contact surface area of the junction points is compressed by the force of rolling up the corrugated plates, and the contact surface area can be freely increased or decreased.

Because of this make-up, the exhaust gas which enters from the entrance does not pass through a single pathway, as in the prior art. Its passage straight through the catalyst is impeded by the intersecting pathways and it is mixed and dispersed in the converter as it collides repeatedly with the catalyst walls. Therefore, an almost completely uniform catalyst treatment can be achieved.

Furthermore, the heat can be freely dispersed by

changing the angle of intersection between the central and outer parts.

In this second working example, the angle of intersection is ordinarily less than 45°, and preferable 3-10°.

In particular, in this invention, the second working embodiment includes the case in which the stainless steel itself is made into this embodiment. The means (a) and (b) mentioned above need not be applied, or only one of them may be applied.

Furthermore, in the discussion above the case in which the catalyst is directly supported on the needle-like ceramic crystals was described, but the invention is not limited to this; one may also put a coating layer of gamma alumina or another suitable material over the needle-shaped ceramics, and support the catalyst on it.

Effects of the Invention

This invention provides a novel metal support for a catalyst, and its industrial use has great effectiveness.

4. Simple Explanation of Drawings:

Fig. 1 is an example of a monolith-type catalytic converter of this invention; Fig. 2 is an explanatory drawing of a honeycomb metal support; Fig. 3 is an explanatory drawing of a honeycomb metal support substrate; Fig. 4 is an explanatory drawing of a metal support with

needle-shaped mullite [crystals] formed on it; and Figs. 5-7 are explanatory drawings showing other examples of catalyst supports.

1 ... converter
2 ... metal support
3 ... flat plate
4 ... corrugated plate
5 ... substrate
6 ... whiskers
7 ... gap
30 ... corrugated plate
31 ... corrugated plate
32 ... flat plate

Applicant: Matsumoto Tekkan Co., Ltd.
Agent: Noboru Okabe, Patent Attorney

Fig. 1

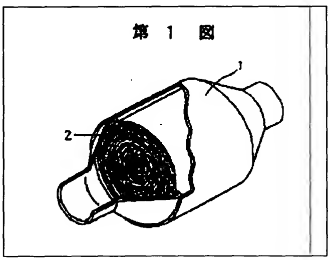

Fig. 2

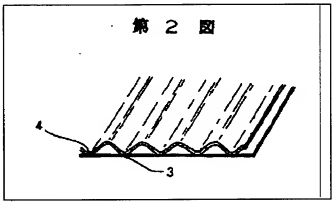

Fig. 3

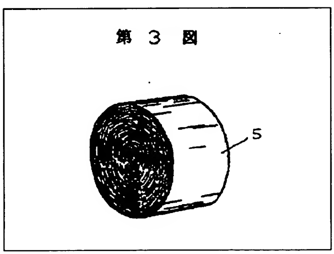

Fig. 4

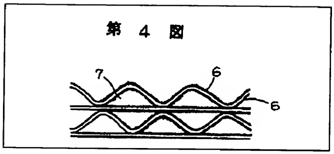

Fig. 5

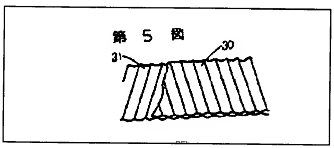

Fig. 6

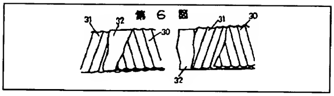

Fig. 7